PATENT COUPERATION TREATY

To:

From the INTERNATIONAL BUREAU

PCT	To:
NOTIFICATION OF ELECTION (PCT Rule 61.2)	Assistant Commissioner for Patents United States Patent and Trademark Office Box PCT Washington, D.C.20231 ETATS-UNIS D'AMERIQUE
Date of mailing (day/month/year) 30 August 2000 (30.08.00)	in its capacity as elected Office
International application No. PCT/EP00/00357	Applicant's or agent's file reference 95.0114
International filing date (day/month/year) 13 January 2000 (13.01.00)	Priority date (day/month/year) 16 January 1999 (16.01.99)
SAWDON, Christopher et al	
1. The designated Office is hereby notified of its election made X in the demand filed with the International Preliminary 31 July 2000 (3 in a notice effecting later election filed with the International Preliminary 31 July 2000 (3 was was was not made before the expiration of 19 months from the priority de Rule 32.2(b).	Examining Authority on: 1.07.00) ational Bureau on:
	Authorized officer

Form PCT/IB/331 (July 1992)

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

	icant's or agent's file reference FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IF		ee Notification of Transmittal of International reliminary Examination Report (Form PCT/IPEA/416)
NO 95.01		International filing date (day/month/year	
	application No.	13/01/2000	16/01/1999
PCT/EP0	<u> </u>		
nternational 009K7/06		or national classification and IPC	
Applicant			
•	H N.V. et al.		
<u> </u>			U. J. Dallering at Everning Authority
1. This in	ternational preliminary ex	kamination report has been prepared by ant according to Article 36.	this International Preliminary Examining Authority
andis	transmitted to the applied	in addording to historic co.	
o This 🗆	EPORT consists of a total	al of 6 sheets, including this cover sheet	t.
□ TI	his report is also accomp	anied by ANNEXES, i.e. sheets of the de	escription, claims and/or drawings which have
be /-	een amended and are the	e basis for this report and/or sheets conta on 607 of the Administrative Instructions	aining rectifications made before this Authority under the PCT).
(S	ee Rule 70. It and Section	MI 007 Of the Administrative mendenens	
These	annexes consist of a tot	al of sheets.	
	<u></u>		
		to the state of the state of the same of	
3. This r	eport contains indications	relating to the following items:	
1	☑ Basis of the report		
11	Priority		
Ш	Non-establishment	t of opinion with regard to novelty, invent	tive step and industrial applicability
IV	☐ Lack of unity of inv		
V	Reasoned statement citations and explain	ent under Article 35(2) with regard to nov inations suporting such statement	velty, inventive step or industrial applicability;
VI	☑ Certain document		
VII	Certain defects in	the international application	
VIII	🖾 Certain observatio	ns on the international application	
Date of sub	omission of the demand	Date of con	npletion of this report
.		19.01.2001	
31/07/20	00	19.01.2001	
	mailing address of the intern	ational Authorized	officer officer
preliminary	examining authority: European Patent Office		
91)	D-80298 Munich	olde Sche	eper, B
١	Tel. +49 89 2399 - 0 Tx: 5	23656 epmu d	St. Merce Ell Mary

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00357

I. Basis of the report

1.	resp the i	onse to an invitation	awn on the basis of (substitute sheets which have been furnished to the receiving Office in under Article 14 are referred to in this report as "originally filed" and are not annexed to not contain amendments (Rules 70.16 and 70.17).):
	1-8	6	as originally filed
	Clai	ms, No.:	
	1-11	1	as originally filed
2.	With lang	n regard to the lang guage in which the ir	uage, all the elements marked above were available or furnished to this Authority in the nternational application was filed, unless otherwise indicated under this item.
	The	se elements were a	vailable or furnished to this Authority in the following language: , which is:
		the language of a t	ranslation furnished for the purposes of the international search (under Rule 23.1(b)).
		the language of pu	blication of the international application (under Rule 48.3(b)).
			ranslation furnished for the purposes of international preliminary examination (under Rule
3.	Witl inte	n regard to any nuc rnational preliminan	leotide and/or amino acid sequence disclosed in the international application, the yexamination was carried out on the basis of the sequence listing:
		contained in the in	ternational application in written form.
		filed together with	the international application in computer readable form.
		furnished subsequ	ently to this Authority in written form.
		furnished subsequ	ently to this Authority in computer readable form.
		the international ap	t the subsequently furnished written sequence listing does not go beyond the disclosure in pplication as filed has been furnished.
		The statement tha listing has been fu	t the information recorded in computer readable form is identical to the written sequence rnished.
4.	. The	e amendments have	e resulted in the cancellation of:
		the description,	pages:
		the claims,	Nos.:
		the drawings,	sheets:
5	. 🗆	This report has be	en established as if (some of) the amendments had not been made, since they have been beyond the disclosure as filed (Rule 70.2(c)):



International application No. PCT/EP00/00357

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

- 6. Additional observations, if necessary:
- V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

Novelty (N)

Yes:

No:

Claims 2,5,7-9

Claims 1,3,4,6,10,11

Inventive step (IS)

Yes:

No:

Claims

Claims

Claims 1-11 No:

Industrial applicability (IA)

Yes:

Claims 1-11

- 2. Citations and explanations see separate sheet
- Certain documents cited VI.
- 1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: Calloni, G. et al; "Carbon Black, A Low Cost Colloidal Additive for Controlling Gas-Migration in Cement Slurries"; SPE International Symposium on Oilfield Chemistry; San Antonio, Texas, USA; 14-17 February 1995; SPE 28959; XP-000915655

D2: US-A-4 012 329

D3: US-A-4 689 161

D4: EP-A-0 449 257

D5: Encyclopedia of Polymer Science and Engineering; Mark, H.F. et al, editors; John Wiley & Sons, New York; Vol. 2, "Carbon Black", pages 623-637

- 1. The present application relates to a electrically conductive invert emulsion wellbore fluid (claims 1-9), a method for drilling or completing a well (claim 10), and a method of providing enhanced information (claim 11).
- 2. D1 discloses an invert emulsion comprising carbon black and a surfactant (see page 146, 2nd column, 5th paragraph; page 148 "Field Application"; Tables 1-2, slurry "D" and "E". Although no "HLB" values are indicated it is reasonable to assume that said value is below 12.
- 3. D2 discloses the same wellbore fluids as the present applications, but does not cite carbon black particles. It is however indicated that further additives may be added (column 5, lines 24-35).
- 4. D3 discloses tendrillar carbonaceous material (TCM) and carbon black as additives (viscosifiers) for invert drilling fluids. The TCM particle dimensions are comparable with those of carbon black (see column 1, lines 42-55; column 10, line 19 to column 11, line 36; Examples 10, 11, 14; Tables 5, 6, 8-10; Figure 1)
- 5. D4 teaches that carbon black is an usual additive for invert drilling muds (page 4,

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lines 13-15).

- 6. D5 discloses the definition of carbon blacks.
- 7. Thus, the subject-matter of present claims 1, 3, 4, 6, 10, and 11 lacks novelty in view of the cited prior art (Art. 33(2) PCT).
- 8. Even if novelty would be established it remains questionable whether the application involves an inventive step in accordance with Art. 33(3) PCT. Carbon black is an additive which is known in the art as a viscosifier or gas-block additive (D1, D3, D4). Carbon black is also known to impart electrical conductivity to substances (D5, page 633, 3rd paragraph). If document D2 is taken as closest prior art then the objective problem in view of said document would be to provide a further embodiment of the compositions of D2. Adding a known additive in order to provide a further embodiment cannot involve an inventive step. The compositions of the present application do not show any surprising or unexpected effects in view of those of D2.
- 9. It appears that the subject-matter of present claims 2, 5, 7, 8, and 9 does not involve an inventive step since the application on file does not contain any indications, surprising effects or unexpected results by virtue of the distinguishing features in view of the cited prior art (Art. 33(3) PCT).
- 10. The subject-matter of present claims 1-10 satisfies the criterion set forth in Article 33 (4) PCT.

For the assessment of present claims 11 on the question whether it is industrially applicable, no unified criteria exist in the PCT Contracting States. Although said claim is characterized by unclear features it appears that according to its nature, it can be made or used (in the technological sense) in any kind of industry (PCT-Examination Guidelines, C-II, 4.12; Art. 33(1) and (4) PCT, Rule 5.1(a)(vi) PCT).

Re Item VI
Certain documents cited

INTERNATIONAL PRELIMINARY



International application No. PCT/EP00/00357

EXAMINATION REPORT - SEPARATE SHEET

Certain published documents (Rule 70.10)

Application No. Patent No

Publication date (day/month/year)

Filing date (day/month/year) Priority date (valid claim) (day/month/year)

EP-A-0 902 076

17.03.1999

02.09.1998

12.09.1997

This document discloses electrical well logging in which carbon type fibres or flakes (see paragraphs [0033-0035]) are added to a non-conductive fluid.

Re Item VIII

Certain observations on the international application

- Claim 11 is unclear because said claim does not describe an actual method (Art. 6 1. PCT; PCT Examination Guidelines C-III-3.1).
- The feature "and the like" used in claim 11 is undefined and therefore unclear (Art. 2. 6 PCT).
- It appears that claim 11 expresses only a mere whish. 3.



(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 95.0114		of Transmittal of International Search F 220) as well as, where applicable, item	•				
International application No.	International filing date (day/month.year)	(Earliest) Priority Date (day/month/	(year)				
PCT/EP 00/00357 13/01/2000 16/01/1999							
SOFITECH N.V. et al.							
according to Article 18. A copy is being t This International Search Report consist	en prepared by this International Searching Autransmitted to the International Bureau. Is of a total of3 sheets. By a copy of each prior art document cited in this		ant				
Basis of the report							
	e international search was carried out on the ba nless otherwise indicated under this item.	isis of the international application in th	ne				
the international search Authority (Rule 23.1(b)).	was carried out on the basis of a translation of	the international application furnished	to this				
was carried out on the basis of t contained in the internat filed together with the in furnished subsequently furnished subsequently the statement that the subsequent international application	Ind/or amino acid sequence disclosed in the in the sequence listing: ional application in written form. Iternational application in computer readable for to this Authority in written form. Ito this Authority in computer readble form. In the sequence listing as filed has been furnished. Information recorded in computer readable form.	m. does not go beyond the disclosure in th	he				
2. Certain claims were fo	und unsearchable (See Box I).						
3. Unity of invention is la	3. Unity of invention is lacking (see Box II).						
	submitted by the applicant. ished by this Authority to read as follows:						
the text has been establ	submitted by the applicant. ished, according to Rule 38.2(b), by this Authone he date of mailing of this international search re						
	blished with the abstract is Figure No.		,				
as suggested by the app	•	\overline{X} None of the fi	igures.				
because the applicant fa	illed to suggest a figure.						
because this figure bette	er characterizes the invention.						

International Application No

P 00/00357

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09K

Documentation searched other than min mum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.				
CALLONI G. ET AL; "Carbon Black: A Low Cost Colloidal Additive for Controlling Gas-Migration in Cement Slurries"; SPE International Symposium on Oilfield Chemistry; San Antonio, Texas, USA; 14-17 February 1995; SPE 28959 XP000915655 page 146, column 2, paragraph 5 page 148, column 2, paragraph 2; tables	1-6,10,				
1,2	1-11				
US 4 012 329 A (HAYES JOHN B ET AL) 15 March 1977 (1977-03-15) column 5, line 24 - line 35	1-11				
	CALLONI G. ET AL; "Carbon Black: A Low Cost Colloidal Additive for Controlling Gas-Migration in Cement Slurries"; SPE International Symposium on Oilfield Chemistry; San Antonio, Texas, USA; 14-17 February 1995; SPE 28959 XP000915655 page 146, column 2, paragraph 5 page 148, column 2, paragraph 2; tables 1,2 US 4 012 329 A (HAYES JOHN B ET AL) 15 March 1977 (1977-03-15) column 5, line 24 - line 35				

Σ Further documents are listed in the continuation of box C.	Patent family members are listed in annex.		
"A" document defining the general state of the lart which is not considered to be of particular relevance."	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier document but published on or after the international filling date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (all specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filling date but later than the priority date claimed	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 16 June 2000	Date of mailing of the international search report $06/07/2000$		
Name and mailing address of the ISA European Patent Office P.B. 5818 Patentlaan 2 NL = 228C HV Rijswijk Tel. (+31=70) 340=2040, Tx. 31 651 epo nl, Fax: (+31=70) 340=3016	Authonzed officer olde Scheper, B		

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Information on patent family members

International Application No
PC 00/00357

Patent document cited in search repor	t	Publication date	Patent family member(s)	Publication date
US 4012329	A	15-03-1977	NONE	
US 4689161	Α	25-08-1987	AT 76119 T AU 593248 B AU 5729186 A BR 8602338 A CA 1302029 A DE 3685256 A EP 0202940 A JP 1633974 C JP 2057837 B JP 62030178 A KR 9309246 B US 4735733 A US 4743431 A ZA 8603570 A	15-05-1992 08-02-1990 27-11-1986 21-01-1987 02-06-1992 17-06-1992 26-11-1986 20-01-1992 06-12-1990 09-02-1987 24-09-1993 05-04-1988 10-05-1988
EP 0449257	A	02-10-1991	US 5068041 A AT 154627 T AU 638563 B AU 7398191 A CA 2039490 A DE 69126558 D DK 449257 T EP 0764711 A NO 176360 B US 5869433 A US 5189012 A US H1000 H	26-11-1991 15-07-1997 01-07-1993 03-10-1991 01-10-1997 24-07-1997 29-12-1997 26-03-1997 12-12-1994 09-02-1999 23-02-1993
EP 0902076	A	17-03-1999	US 6006831 A CA 2244409 A NO 984150 A	28-12-1999 12-03-1999 15-03-1999

PC 00/00357

C.(Continuation) DOCUMENTS CONSIDERED OBE REL Category Citation of document, with indication, where appr	<u> </u>	
l .	ophate, or the relevant passages	Relevant to claim No.
Y US 4 689 161 A (BLUMENT 25 August 1987 (1987-08 column 1, line 42 - lin column 10, line 19 -col figure 1; examples 10,1 5,6,8-10	-25) e 55 umn 11, line 36;	1-11
A MARK, H.F. EDITOR: "En Polymer Science and Eng "Carbon Black", pages 6 1985, JOHN WILEY & SON XP002140365	ineering, Vol. 2, 23-637"	1-11
Y EP 0 449 257 A (MI DRIL 2 October 1991 (1991-10 page 4, line 13 - line	-02)	1-11
P,Y EP 0 902 076 A (SOFITEC CIE DOWELL (FR)) 17 March 1999 (1999-03-the whole document		1-11

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INTERNATIONAL APPLICATION PUBLISH	HED I	JNDER THE PATENT COOPERATION TREATY (PCT)
(51) International Patent Classification:		(11) International Publication Number: WO 00/41480
Not classified	A2	(43) International Publication Date: 20 July 2000 (20,07,00)
(21) International Application Number: PCT/EPC	00/003:	[GB/GB]; 7 Menabilly Road, St Austell, Cornwall PL25 4DY (GB).
(22) International Filing Date: 13 January 2000 (10) (30) Priority Data: 9900904.5 16 January 1999 (16.01.99)	13.01.0 G	(74) Agent: MENES, Catherine; Etudes et Productions Schlum- berger, Division Dowell, 26, rue de la Cavée, BP 202, F-92142 Clamart Cedex (FR).
(71) Applicant (for all designated States except CA FR US ITECH N.V. [BE/BE]; Rue de Stalle 142, B-1180 (BE).	S): SOI Brusse	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI,
(71) Applicant (for CA only): SCHLUMBERGER CANAL ITED [CA/CA]; 24th Floor, Monenco Place, 801 enue, S.W., Calgary, Alberta T2P 3W2 (CA).	OA LIM 6th Av	SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW,
(71) Applicant (for FR only): COMPAGNIE DES SEI DOWELL SCHLUMBERGER [FR/FR]; 50, Jean-Jaurès, F-92541 Montrouge (FR).	R VICE avenu	ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI
(72) Inventors; and (75) Inventors/Applicants (for US only): SAWDON, Chr [GB/GB]; 6 Southview Road Biscovey, Par, Comwa 2HJ (GB). TEHRANI, Mostafa [GB/GB]; 41 T Road, St. Austell, Comwall PL25 5AL (GB). CRAD Paul [GB/GB]; 193 Creak-A-Vose Park, St Step Austell, Comwall PL26 7ND (GB). LAWSON, A	all PL2 Frenanc DOCK Shen, S	Without international search report and to be republished upon receipt of that report.

(54) Title: ELECTRICALLY CONDUCTIVE NON-AQUEOUS WELLBORE FLUIDS

(57) Abstract

A wellbore fluid having a non-aqueous continuous liquid phase that exhibits an electrical conductivity increased by a factor in order of 104 to 107 compared to conventional invert emulsion comprises from about 0.2 % to about 10 % by volume of carbon black particles, and one or more emulsifying surfactant(s) selected from the class including: nonionic emulsifiers of Hydrophilic-Lipophilic Balance (HLB) less than about 12, and anionic surfactants wherein the counter-ion (cation) is any of alkali metal, ammonium, or hydrogen ions. This wellbore fluid can be used for drilling or completing a well and can be used for providing enhanced information from electrical logging tools, measurement while drilling, logging while drilling, geosteering and the like.

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PCT/EP00/00357

Electrically Conductive Non-Aqueous Wellbore Fluids

This invention relates to non-aqueous wellbore fluids and in particular concerns wellbore fluids which are electrically conductive. The invention also relates to the use of said wellbore fluids for drilling or completing subterranean wells such as oil and gas wells.

In the process of rotary drilling a well, a drilling fluid or mud is circulated down the rotating drill pipe, through the bit, and up the annular space between the pipe and the formation or steel casing, to the surface. The drilling fluid performs different functions. It removes cuttings from the bottom of the hole to the surface, suspends cuttings and weighting material when the circulation is interrupted, controls subsurface pressure, isolates the fluids from the formation by providing sufficient hydrostatic pressure to prevent the ingress of formation fluids into the wellbore, cools and lubricates the drill string and bit, maximises penetration rate etc. An important objective in drilling a well is also to secure the maximum amount of information about the type of formations being penetrated and the type of fluids or gases in the formation. This information is obtained by analysing the cuttings and by electrical logging technology and by the use of various downhole logging techniques, including electrical measurements.

The required functions can be achieved by a wide range of fluids composed of various combinations of solids, liquids and gases and classified according to the constitution of the continuous phase mainly in two groupings: aqueous (water-based) drilling fluids, and non-aqueous (mineral oil or synthetic-base) drilling fluids, commonly called 'oil-based fluids'.

Water-based fluids constitute the most commonly used drilling fluid type. The aqueous phase is made of fresh water or, more often, of a brine. As discontinuous phases, they may contain gases, water-immiscible fluids such as diesel oil to form an oil-in-water emulsion, and solids including clays and weighting material such as barite. The properties are typically controlled by the addition of clay minerals, polymers and surfactants.

In drilling water-sensitive zones such as reactive shales, production formations or where bottom hole temperature conditions are severe or where corrosion is a major problem, oil-based drilling fluids are preferred. The continuous phase is a mineral or synthetic oil and commonly contains water or brine as discontinuous phase to form a water-in-oil emulsion or invert emulsion. The solid phase is essentially similar to that of water-based fluids and these fluids too contain several additives for the control of density, rheology and fluid loss. The invert emulsion is formed and stabilised with the aid of one or more specially selected emulsifiers.

Although oil-based drilling fluids are more expensive than water-based muds, it is on the basis of the added operational advantage and superior technical performance of the oil-based fluids that these are often used for the drilling operations.

An area where oil-based muds have been at a technical disadvantage, because of their very low electrical conductivity, is in electrical well-logging. Various logging and imaging operations are performed during the drilling operation, for example while drilling in the reservoir region of an oil/gas well in order to determine the type of formation and the material therein. Such information may be used to optimally locate the pay zone, i.e. where the reservoir is perforated in order to allow the inflow of hydrocarbons to the wellbore.

Some logging tools work on the basis of a resistivity contrast between the fluid in the wellbore (drilling fluid) and that already in the formation. These are known as resistivity logging tools. Briefly, alternating current flows through the formation between two electrodes. Thus, the fluids in the path of the electric current are the formation fluids and the fluid which has penetrated the formation by way of filtration. The filtercake and filtrate result from filtration of the mud over a permeable medium (such as formation rock) under differential pressure.

Another example where fluid conductivity plays an important part in the drilling operation is in directional drilling where signals produced at the drill assembly have to be transmitted through an electrically conductive medium to the control unit and/or mud telemetry unit further back on the drill string.

At present the use of resistivity logging tools is limited mainly to cases where a water-based drilling fluid is used for the drilling operation (the very low conductivity of the base-oil in the case of oil/synthetic-base muds precludes the use of resistivity tools in such fluids). Although the brine dispersed in the oil phase is electrically conductive, the discontinuous nature of the droplets prevents the flow of electricity. Indeed, the inability of these emulsions to conduct electricity (until a very high potential difference is applied) is used as a standard test of emulsion stability. To that extent it is worth bearing in mind that the electrical conductivity of the oil base is typically in the range 10^{-6} to $5 \times 10^{-2} \mu \text{S.m}^{-1}$ at a frequency of 1 kHz while an electrical conductivity of not less than $10 \mu \text{S.m}^{-1}$ and preferably of no less than $10^{3}\mu \text{S.m}^{-1}$ is desirable for electrical logging operations. So there is a need to increase the electrical conductivity of the fluid by a factor in the order of 10^{4} to 10^{7} .

A few attempts to make oil-based drilling fluids electrically conductive for the purpose of electrical logging have been reported though none of them has been a commercial success. U.S. Patent No. 2,542,020, U.S. Patent No. 2,552,775, U.S. Patent No. 2,573,961, U.S. Patent No. 2,696,468 and U.S. Patent No. 2,739,120, all to Fischer, disclose soap-stabilised oil-based

fluids comprising an alkaline-earth metal base dissolved in up to 10% by weight water. Fischer claims to reduce the electrical resistivity to below 500 ohm-m which corresponds to an increase of conductivity to $\kappa > 2000~\mu S~m^{-1}$. However, those fluids happen to be very sensitive to contaminants and greater amounts of water lead to unacceptable increase of the fluid loss. In essence these fluids relied on the residual or added water content to dissolve the salts/surfactants. Moreover, the continuous oil phase fails to exhibit any increase of its electrical conductivity and there is no reference to what happens to the filtrate which under optimum conditions is made up essentially of the continuous oil phase.

Twenty five years later, U.S. Patent 4, 012,329 disclosed an oil-external micro-emulsion made with sodium petroleum sulfonate and reported of resistivity < 1 ohm-m ($\kappa > 1$ S m⁻¹). In such a micro-emulsion, the sodium petroleum sulfonate forms micelles that contain water and the clay so that the clay has to be added as a dispersion in water and cannot be added as dry powder. It should be also emphasised that a micro-emulsion is distinctly different from a standard emulsion, being thermodynamically stable, smaller in size, higher in surface to volume ratio and forming both filtercakes and fluid filtrate of a different nature. Obtaining the necessary combination of bulk properties and non-damaging rock interactions is more difficult than for a standard direct or invert emulsion fluid, and such fluids are not generally favoured for drilling oil wells.

Although the prior art contains formulations for making oil-based drilling fluid conductive, the methods so described adversely affect other mud properties, another reason why none have been successfully commercialised.

The aim of this invention is thus to provide a non-aqueous wellbore fluid which exhibits a substantial electrical conductivity.

When mixed in an article at sufficient concentrations, carbon black is known to impart electrical conductivity to otherwise insulating materials such as plastics or elastomers. The extremely small carbon black particles (<< 1 micron) are known to form an interconnecting network which allows the conduction of electricity. Such articles can thus, for instance, avoid the build up of static electricity or shield against electromagnetic interference.

However, when carbon black was added to a conventional invert emulsion oil-based drilling fluid or mud (hereinafter referred to as OBM), little or no useful increase in conductivity was observed.

More specifically it has been found that the calcium soaps of fatty acids such as tall oil fatty acid will interact with the network of carbon particles, decreasing the particle-particle attractive forces by adsorbing onto the particles. Similarly, invert emulsifiers or wetting agents having

primary, secondary, tertiary amine groups or quaternary ammonium groups have been found to adsorb similarly and disrupt the conductive network of carbon black particles. Examples of such amine-containing products include fatty alkyl amidoamines, fatty alkyl imidazolines, fatty alkylamidoamines further reacted or cross-linked with di- or tri-basic acids such as maleic acid. Such calcium fatty acid soaps and amine-functional products are in very common use in all invert emulsion drilling fluids known to the applicants.

This invention has discovered that when carbon black is mixed in an OBM containing certain types of emulsifiers and oil-wetting agents, high levels of electrical conductivity can be obtained at advantageously low concentrations of carbon black.

Surprisingly, it has been found that in spite of the very high surface area and adsorption capacity of carbon black, certain invert emulsifiers and oil-wetting agent types do not disrupt the electrically conductive carbon black network.

In accordance with the invention, an electrically conductive invert emulsion wellbore fluid comprises from about 0.2% to about 10% by volume of carbon black particles and one or more emulsifying surfactant(s) selected from the class including: nonionic emulsifiers of Hydrophilic-Lipophilic Balance (HLB) less than about 12, and anionic surfactants wherein the counter-ion (cation) is any of alkali metal, ammonium, or hydrogen ions

All non-ionic surfactants found to date of an Hydrophilic-Lipophilic Balance (HLB) suitable to promote invert emulsification, do not destroy the conductivity. These include the diethanolamides based on higher fatty acids of more than 12 carbon atoms such as oleic acid or tall oil fatty acid (TOFA), alkoxylated higher fatty alcohols, alkoxylated alkylphenols, and ethylene oxide/propylene oxide block polymers. Generally, the more suitable HLB values are less than 10, but occasionally in combination with other emulsifiers, higher HLB values up to a maximum of 12 can be useful.

The other suitable classes of surfactants are anionic surfactants of sufficiently lipophilic character where the anionic surfactant is in the form of an alkali metal soap, the ammonium soap, or as the free acid. Polyvalent metal ion (e.g. calcium) soaps of these anionic surfactants are excluded because they have been found to disrupt the conductive network of carbon black particles, presumably by adsorption through ion-bridging by the polyvalent cation. The most preferred anionic surfactants are sulphonates such as alkane sulphonates, alpha-olefin sulphonates, alkylarene sulphonates, polyolefin sulphonates, and acyl taurates, all characterised by the carbon number of the hydrophobic moiety being at least about 12.

Other suitable anionic emulsifiers or wetting agents include the alkali metal or ammonium salts, or the free acid of fatty acids of 12 or more carbon atoms, phosphate esters of ethoxylated

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alcohols of 12 or more carbon atoms, phosphate esters of ethoxylated alkylphenols of 14 or more carbon atoms, and alkylaminomethylene phosphonic acids wherein the alkylamine precursor contains 12 or more carbon atoms.

The total dose of emulsifiers is preferably in the range of 0.5% to 10%, based on the total weight of the wellbore fluid.

A preferred carbon black in this invention has a significantly higher specific surface area (i.e. at least 500 m²/g) than the conventional carbon black. A very suitable grade has a specific surface area of about 1500 m²/g compared to 100-300 m²/g of the conventional black. This gives the carbon black particles a higher ability to form an interconnecting network of particles which leads to a thixotropic rheological effect and a significant increase in conduction of electricity.

The most important attribute of this invention is that the electrical conductivity of the fluid is increased by a factor of the order of 10⁴ to 10⁷. This allows the successful application of many electrical logging techniques and the transmission of electrical telemetry signals when organic liquid-based wellbore fluids fill the borehole. Another object of the present invention is therefore a method of providing enhanced information from electrical logging tools, measurement-while-drilling (MWD), logging-while-drilling (LWD), geosteering and the like wherein the efficiency is enhanced by the improved electrical conductivity wellbore fluids of the invention.

In this invention it has been found that electrically conductive, oil-based drilling fluids can be provided which maintain the performance advantages expected from known oil-based (or synthetic organic liquid-based) drilling fluids. Therefore, the fluids of this invention minimise adverse interactions with drilled rock formation, such as clay formation swelling or dispersion, hole collapse, or the undesirable dissolution of underground salt formations. They also provide the performance advantages expected from oil-based fluids with regard to enhanced lubricity, reduced differential sticking of drill pipe, and good stability at high temperatures.

According to a preferred embodiment of the present invention, the wellbore fluid also comprises material capable of precipitating or complexing polyvalent metal cations such as the ions of calcium, magnesium and iron which may contaminate the wellbore fluid. This is to prevent the metal cation from forming a soap with emulsifiers which then adsorbs on the surface of carbon black particles and interferes with the conductive network.

Examples of precipitating materials are dissolved anions such as phosphate, carbonate or silicate. Examples of suitable complexing agents are the alkali metal or ammonium salts, or the free acids, of citric acid, gluconic acid, glucoheptanoic acid, ascorbic acid, erythorbic acid, nitrolotriacetic acid, ethylene diamine tetraacetic acid, diethylenetriamine pentaacetic acid,

hydroxyethylidene diphosphonic acid, nitrolotrismethylenephosphonic acid, aminomethylene phosphonates based on ethylene diamine or diethylene triamine or higher ethyleneamines, and polyphosphates such as tetrasodium pyrophosphate

The continous non aqueous phase may be selected from any refined or synthetic fluid known to be suitable as a wellbore fluid base liquid such as crude oil, hydrocarbon refined fractions from crude oil such as diesel fuel or mineral oil, synthetic hydrocarbons such as n-paraffins, alphaolefins, internal olefins, and poly-alphaolefins; synthetic liquids such as dialkyl ethers, alkyl alkanoate esters, acetals; and natural oils such as triglycerides including rape-seed oil, sunflower oil and mixtures thereof. Low toxicity and highly biodegradable oils will be generally preferred especially for offshore drilling.

The discontinuous liquid phase is water or a brine and is present from about 0.5% to about 70% by volume of the emulsion.

In order to provide other properties required from wellbore fluids, the wellbore fluids of this invention may further contain any known wellbore fluid additives such as clay, organoclay, or polymeric viscosifiers, filtration reducers such as lignite derivatives or powdered gilsonite filtration reducers, asphalts, asphaltites or polymers swollen by the oil, weighting agents such as finely divided barytes or hematite, lubricating additives, or any other functional additive known to those skilled in the art. These additives aim to provide a drilling mud that has the following characteristics:

- be fluid and produce affordable pressure drop in surface pipes and drill string
- have a yield stress suitable for supporting/transporting mud solids and drill cuttings
- be chemically, thermally and mechanically stable
- provide hole stability
- provide good lubricity
- prevent excessive fluid loss to the formation

The invention will now be illustrated by the following examples.

Example 1.

This example demonstrates the effectiveness of carbon black in increasing the electrical conductivity of a non-conductive mineral oil (Surdyne B140). The conductivity of the oil is below $1 \mu S/m$.

We prepared a 1.5% by weight dispersion of carbon black in the mineral oil. The carbon black particles form irregular-shaped aggregates of extremely fine carbon particles fused together.

The size of the aggregates is in the range 10-250 nm but the larger aggregates may be reduced in size by mechanical shearing. The conductivity of the oil-carbon black dispersion was about $20000 \, \mu\text{S/m}$ at 500Hz and at room temperature.

Example 2.

In this example we show the effect of carbon black addition on the conductivity of an oil-based mud using a conventional tall oil fatty acid calcium soap as the emulsifier:

Table 1. Formulation for a weighted mud with conventional fatty acid invert emulsifier: oil/water ratio:80/20.

Components	Amount in 350ml of mud		
Mineral oil (Surdyne B140)	183.3 g		
Tall oil fatty acid	9.0 g		
Fluid loss additive (TRUFLO 100™)	4.5 g		
Lime	5.0 g		
Carbon black	6.0 g		
Sodium chloride	22.67 g		
Water	63.2 g		
Barite	131.2 g		

The conductivity of the full mud formulation is reduced to about 15 μ S/m at 500Hz. The results suggest that a conventional soap of tall oil fatty acid emulsifier (as used in almost all conventional oil-based mud formulations) does not allow the conductive network of carbon black particles to form. This is ascribed to strong adsorption of the calcium neutralised emulsifier on the carbon black particles, inhibiting the particle-particle interactions which form the network.

Example 3.

Effect of carbon black on the electrical conductivity of an oil-based mud which uses fatty acid diethanolamides (WITCAMIDE 511, a product of WITCO) as the emulsifier:

Table 2. Formulation for a weighted conductive OBM: oil/water ratio: 80/20

Components	Amount for 350ml of mud		
Mineral Oil (Surdyne B 140)	182.3 g		
Non-ionic emulsifier	8.0 g		
Alpha-olefin sulphonate emulsifier	1.0 g		
Fluid loss additive (TRUFLO 100™)	4.5 g		
Carbon black	6.0 g		
NaCl	21.43 g		
Water	59.75 g		
Barite	131.1 g		

The conductivity of the above formulation was $10,000~\mu\text{S/m}$ at 500Hz in the full mud formulation. It can be seen that this emulsifier type allows the carbon black conductive network (and hence conductivity) to be maintained, whilst imparting good emulsion stability, even in a weighting fluid where the barite has a diluting effect on the conductive network and reduces the conductivity to some extent. The function of the alpha-olefin sulphonate in the formulation is to improve the oil-wetting of barite.

CLAIMS

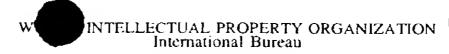
- 1. An electrically conductive invert emulsion wellbore fluid comprising:
 - i) from about 0.2% to about 10% by volume of carbon black particles, and
 - one or more emulsifying surfactant(s) selected from the class including: nonionic emulsifiers of Hydrophilic-Lipophilic Balance (HLB) less than about 12, and anionic surfactants wherein the counter-ion (cation) is any of alkali metal, ammonium, or hydrogen ions.
- 2. A wellbore fluid according to Claim 1 wherein the carbon black exhibits a specific surface area of at least 500 m²/g, and preferably of at least 1500 m²/g.
- 3. A wellbore fluid according to any preceding Claim wherein the nonionic emulsifier(s) is (are) selected from the class including: diethanolamides based on fatty acids of more than 12 carbon atoms, alkoxylated fatty alcohols, alkoxylated alkylphenols, and ethylene oxide propylene oxide block polymers.
- 4. A wellbore fluid according to any preceding Claim wherein the anionic surfactant(s) is (are) selected from the class including: alkane sulphonates, alpha olefin sulphonates, alkyl arene sulphonates, polyolefin sulphonates and acyl taurates, all characterised by the carbon number of the hydrophobic moiety being at least about 12, and by the counter-ion (cation) being any of alkali metal, ammonium, or hydrogen ions.
- 5. A wellbore fluid according to any one of Claims 1 to 4 wherein the anionic surfactant(s) is (are) selected from the class including: fatty acids of 12 or more carbon atoms, phosphate esters of ethoxylated alcohols of 12 or more carbon atoms, phosphate esters of ethoxylated alkyl phenols of 14 or more carbon atoms, and alkyl aminomethylene phosphonates wherein the alkylamine precursor contains 12 or more carbon atoms, all characterised by the counter-ion (cation) being any of alkali metal ion, ammonium, or hydrogen ions.
- 6. A welbore fluid according to any preceding Claim in which the total dose of emulsifier(s) is in the range 0.5% to 10% by weight.
- 7. A wellbore fluid according to any preceding Claim containing any material capable of precipitating or complexing polyvalent metal cations such as the ions of calcium, magnesium and iron.

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- 8. A wellbore fluid according to Claim 8 wherein the emulsified brine phase contains dissolved anions such as phosphate, carbonate, silicate which will form insoluble precipitates with any ions of calcium, magnesium or iron cations.
- 9. A wellbore fluid according to Claim 8 wherein the complexing agent is selected from the class including the alkali metal or ammonium salts, or the free acids, of citric acid, gluconic acid, glucoheptanoic acid, ascorbic acid, erythorbic acid, nitrolotriacetic acid, ethylene diamine tetraacetic acid, diethylenetriamine pentaacetic acid, hydroxyethylidene diphosphonic acid, nitrolotrismethylenephosphonic acid, aminomethylene phosphonates based on ethylene diamine or diethylene triamine or higher ethyleneamines, and polyphosphates such as tetrasodium pyrophosphate.
- 10. A method of drilling or completing a well wherein the wellbore fluid used is as in any preceding Claim.
- 11. A method of providing enhanced information from electrical logging tools, measurement-while-drilling (MWD), logging-while-drilling (LWD), geosteering and the like wherein the efficiency is enhanced by the improved electrical conductivity of any of the wellbore fluids as in Claims 1 to 9.

PCT







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(57) Abstract

A wellbore fluid having a non-aqueous continuous liquid phase that exhibits an electrical conductivity increased by a factor in order of 10⁴ to 10⁷ compared to conventional invert emulsion comprises from about 0.2 % to about 10 % by volume of carbon black particles, and one or more emulsifying surfactant(s) selected from the class including: nonionic emulsifiers of Hydrophilic-Lipophilic Balance (HLB) less than about 12, and anionic surfactants wherein the counter-ion (cation) is any of alkali metal, ammonium, or hydrogen ions. This wellbore fluid can be used for drilling or completing a well and can be used for providing enhanced information from electrical logging tools, measurement while drilling, logging while drilling, geosteering and the like.